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Journal

Journal of Geophysical Research Atmospheres, 103(D11)

ISSN

0148-0227

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Publication Date

1998-06-20

DOI

10.1029/97JD01715

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Peer reviewed

Spatial and temporal variability of nonmethane hydrocarbon mixing ratios and their relation to photochemical lifetime

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Abstract. The relationship between temporal and spatial variability of C₂–C₈ nonmethane hydrocarbon mixing ratios and their HO lifetimes (τ) is presented for samples collected during the 1993 North Atlantic Regional Experiment (NARE) and from other urban and remote sites. The C₂–C₄ alkanes, acetylene and benzene typically define a trend of the form $s_{\ln x} = A\tau^{-b}$ where $s_{\ln x}$ is the standard deviation of the ln of the mixing ratio. The relationship extended over a wider range of hydrocarbons in winter. The exponent b ranged in value from 0.28 ± 0.023 for winter urban data where C₂–C₈ hydrocarbons defined a strongly correlated trend, to 0.56 ± 0.15 for C₂–C₄ hydrocarbons at a coastal site in Nova Scotia during NARE. The trends are significantly different from that given by the Junge relationship [Junge, 1974]. Data from the Azores do not display such a trend and were likely influenced by local emissions. Variance trends are a useful analytical tool for examining the validity of hydrocarbon measurements.

Introduction

The relationship between hydrocarbon reactivity and mixing ratio variability in the troposphere has not been widely studied. Intuitively, one expects the most reactive hydrocarbons to exhibit the greatest spatial and temporal variability. An inverse relationship between concentration variability and residence time for relatively long-lived tropospheric trace gases was first described by Junge [1974]. Junge's empirical relationship,

$$\text{RSD} = \frac{0.14}{\tau} \quad (1)$$

where RSD is the relative standard deviation (the standard deviation divided by the mean concentration) and τ is the residence time in years, has been used to estimate the residence time of trace gases from their observed variability [cf. Panshin and Hites, 1994; Mihalopoulos et al., 1991; Thornton et al., 1996]. To our knowledge, the variability of nonmethane hydrocarbons has not been examined with regard to equation (1). Hamrud [1983] has studied the variability-lifetime relationship using a two-dimensional numerical model in which he varied source and sink distributions of trace gases. He concluded that the source/sink configuration strongly influences the spatial variability, with the τ^{-1} dependence

being approached for very long-lived species. The model scenario that best described the physical situation for nonmethane hydrocarbons produced an RSD trend that could be fit by a $\tau^{-0.72}$ dependence. However, the lifetime range examined in the model, 3 weeks to 64 years, is much longer than most hydrocarbon lifetimes considered in this paper.

Several authors have attempted to derive general mathematical relationships between trace gas variability, as expressed by the relative standard deviation, and lifetime [Gibbs and Slinn, 1973; Jaenicke, 1982; Slinn, 1988]. Jaenicke [1982] derived Junge's inverse relationship based on a consideration of the statistics of an exponentially decaying function sampled over a finite period. For species with long lifetimes compared to the sampling interval, RSD was found to be proportional to τ^{-1} ; otherwise an approximate $\tau^{-1/2}$ relation was obtained. Slinn [1988] came to similar conclusions and stressed that the range of travel times sampled compared to the lifetimes of the gases determined whether RSD is proportional to $\tau^{-1/2}$ or τ^{-1} . The functional dependence of RSD on τ described in these studies is similar to those illustrated by Hamrud [1983]. Gibbs and Slinn [1973], however, came to a different conclusion, stating that in the limits where either fluctuations in the production rate or fluctuations in the loss rate alone are considered, then a $\tau^{-1/2}$ dependence would result. These theoretical papers have taken different approaches to the problem: Junge [1974] used a steady state treatment, Jaenicke [1982] considered exponential decay, Gibbs and Slinn [1973] used a stochastic analysis; and have yielded results that are difficult to reconcile and to apply to the real atmosphere.

Jaenicke's [1982] and Slinn's [1988] treatment of the variability problem by considering the statistics of an exponentially decaying function is probably the most intuitive approach to understanding hydrocarbon trends. The exponential paradigm can be improved if we use the standard

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deviation of the \ln of the concentration ($s_{\ln x}$) instead of the relative standard deviation. In the limit of small variability (long τ), RSD equals $s_{\ln x}$, as can be demonstrated by the differential of $\ln(x)$, but at high variability (short τ , as for the hydrocarbons to be considered here), $s_{\ln x}$ gives much simpler behavior.

In the absence of mixing, the \ln -transformed concentration of a hydrocarbon in an air parcel decreases linearly with time as a result of oxidation by HO radicals according to equation (2),

$$\ln\left(\frac{X}{X^0}\right) = -\frac{t}{\tau} \quad (2)$$

where t is the time between emission and sampling, X^0 is the initial concentration, and τ is the $1/e$ lifetime. If a hydrocarbon data set can be approximated as measurements of an ensemble of air parcels with the same X^0 but varying t , then the variance of the log term is given by

$$\sigma_y^2 = \left(\frac{\partial}{\partial t} \ln\left(\frac{X}{X^0}\right)\right)^2 \sigma_t^2 = \left(\frac{-1}{\tau}\right)^2 \sigma_t^2 \quad (3)$$

assuming τ to be constant, so that

$$\sigma_y = s_{\ln x} = \frac{1}{\tau} \sigma_t \quad (4)$$

Equation (4) shows that the standard deviation of the \ln -transformed data is inversely proportional to the $1/e$ lifetime for chemical kinetic conditions. The proportionality constant is the standard deviation of the time distribution. The dependence of RSD on lifetime is a much more complicated function as noted by Jaenicke [1982] and Slinn [1988], and illustrated by Hamrud's [1983] figures, approaching the inverse dependence limit only when the range of travel times is small compared to the lifetime. Their results would have been greatly simplified had they worked from the \ln -transformed point of view.

In this paper, variability patterns of C_2 - C_8 hydrocarbons from the 1993 North Atlantic Regional Experiment (NARE) and other locations are examined to determine to what extent hydrocarbon variability is related to lifetime and how the trends compare to the Junge relation given in (1). Note that Junge's relationship was principally determined from long-lived species with small variances so that their relative standard deviation is equivalent to $s_{\ln x}$. Junge [1974] recognized this equivalence of RSD and $s_{\ln x}$ and used the latter when dealing with H_2O .

Experiment

The hydrocarbon data presented here have been collected from three different research groups over the past several years. Five data sets are from the 1993 North Atlantic Regional Experiment field campaign and have fairly complete coverage of reactive hydrocarbons (C_2 - C_6 alkanes, alkenes, and toluene) ensuring a broad range of lifetimes. The NARE 1993 experiment was conducted in August with hydrocarbon sampling locations and platforms based in the western Atlantic, the Azores, and aboard the ship *Malcolm Baldrige* (see Fehsenfeld et al. [1996] for a description of these locations).

One data set is from an urban area: Boulder, Colorado [Goldan et al., 1995]. A final data set is taken from the Polar Sunrise Experiment 1992 field campaign at Alert, N.W.T., during the "dark" period from January to March [Jobson et al., 1994]. Analysis details for the NARE data sets will be described below, and we refer the reader to the original publications for experimental details of the other data sets.

York University

The York University group analyzed samples collected from Chebogue Point and the Twin Otter aircraft. Air samples were collected into electropolished stainless steel canisters (Biospherics Research Corp., Oregon) pressurized by means of a stainless steel bellows or Teflon diaphragm pump. Canisters were sent to the field evacuated. Sample collection entailed partially filling then venting the canister to condition it before the final sample collection.

Canisters were returned to York for analysis. C_2 - C_7 hydrocarbons were measured using gas chromatography and flame ionization detection. Separation was performed on a 50-m x 0.32-mm Al_2O_3/KCl PLOT column. Sample sizes of 1.5-L were preconcentrated after passing sequentially through a trap filled with 5 g of K_2CO_3 held at 80°C to remove CO_2 and a 15-cm length of Teflon tubing cooled with dry ice to -50°C to further reduce the water content. Ambient samples and standards run through this system showed no losses for C_2 - C_7 alkanes and alkenes, acetylene, benzene, and toluene. Blanks, consisting of ultra pure, hydrocarbon free helium were periodically run between sample analyses. With the exception of benzene these were clean with respect to the lowest concentrations observed, indicating no carryover from the CO_2 and H_2O traps. Benzene contamination was systematic, equivalent to 6 parts per trillion by volume (pptv) for the sample size employed. This blank value, though usually low with respect to ambient levels, was subtracted from the data. Replicate analyses, whereby canisters were reanalyzed a week or two after the first analysis, were performed over the analysis period to validate system and operator performance. Replicate analyses were always within a few percent of each other.

Calibration of individual hydrocarbon responses was done from a parts per billion (ppbv) range gravimetric mixture prepared by Conservation and Protection Services of Environment Canada. Quantification limits (1σ uncertainty equal to 10%) were operationally defined from the observed relation between analysis precision and peak areas of ambient samples and prepared mixtures. Quantification limits vary slightly with hydrocarbon species. For C_5 alkanes the quantification limit for a 1.5-L sample was calculated to be 3 pptv. The lowest observed mixing ratios were 5 pptv, slightly above the quantification limit. This 5 pptv peak yields a signal (peak height) about 10 times greater than the baseline noise width. The corresponding detection limit is 1 pptv. For mixing ratios well above the quantification limit the analysis precision is 1 to 2%.

UC Irvine

The University of California group analyzed samples collected aboard the ship *Malcolm Baldrige* and from ground sites at Sable Island, Nova Scotia and Santa Barbara in the Azores. Ambient whole air samples were collected in 2-L stainless steel canisters fabricated at University of California at

Irvine (UCI). Sample canisters were evacuated to 10^{-2} torr and shipped to the site for sample collection. Although most canisters have shown reliability and stability in the containment of various halocarbons and hydrocarbons, some have also displayed growth of light olefins with time [Blake et al., 1994]. Ambient air rebaking of these canisters has helped to resolve the olefin growth problem.

Samples were analyzed using four Hewlett-Packard 5890 Series II gas chromatographs equipped with flame ionization detectors. A 1200 cm³ (STP) sample was trapped on a glass-bead-filled 1/4 inch stainless steel loop immersed in liquid nitrogen. A flow controller was used to restrict the sample flow to a maximum of 500 mL/min. The total volume sampled was measured by a pressure difference using a pressure transducer. The preconcentration loop was then isolated and warmed to 80°C. When the ovens were at the appropriate temperatures, the sample was injected. The hydrogen carrier flow was split four ways and directed to the following columns: 35% (7 mL/min) to a 50-m, 0.32-mm i.d. Al₂O₃/Na₂SO₄ PLOT column for C₂-C₅ analysis; 25% (5 mL/min) to a 60-m, 0.25-mm i.d., 1-mm film thickness DB-1 column for C₃-C₁₀ detection; 20% (4 mL/min) to a 60-m, 0.25-mm i.d., 0.25-mm film thickness Cyclodex-B column for C₆-C₁₁ analysis; and 20% (4 mL/min) to a 60-m, 0.25-mm i.d., 0.5-mm film thickness DB5-MS column for C₄-C₁₁ separation.

These columns have unique separation characteristics; therefore the elution order of the hydrocarbons on each is quite different. Any co-elution of the reported gases on one column is very likely resolved on another. The time required for one complete cycle of trapping and injecting a sample was 22 min.

The working standard was a partially dried (3 parts per million by volume H₂O) whole air sample contained in an Aculife-treated Luxfer cylinder that was collected at Niwot Ridge, Colorado. Thirty nonmethane hydrocarbons ranging from C₂-C₁₀ present in this standard were requantified using response factors calculated from synthetic standards. The previous calibration values agreed to within 1-5% of the synthetic standards implying that the sample has maintained its integrity in the cylinder.

To monitor the consistency and reproducibility of the analytical system, the working standard was analyzed after every four samples. Although the mixing ratios of the various gases in the working standard had maintained their integrity in the cylinder over time, to further ensure there was no drift in the standard or the system, two other whole air standards were also randomly assayed throughout the project. Mixing ratios of all quantified gases in the standard exhibited no statistically significant changes (1σ) over the period of the project.

Hydrocarbon Lifetimes

Nonmethane hydrocarbons are removed from the atmosphere principally through oxidation initiated by the HO radical. While there is growing evidence that halogen atoms may be important hydrocarbon oxidants in springtime arctic marine boundary layer environments [Jobson et al., 1994; Solberg et al., 1996], a global view suggests that this environment is relatively unimportant compared to overall oxidation in the troposphere [Singh et al., 1996; Rudolph et al., 1996]. However, for sites located in the marine boundary layer the influence of halogen atom chemistry, in particular the influence of atomic chlorine on alkane lifetimes, may be

important enough to warrant consideration in explaining hydrocarbon trends. In this paper we assume hydrocarbon lifetimes are determined by the HO radical. Ozone reaction with olefins is important, in particular in winter when HO radical concentrations are low. However, for midlatitude summers the lifetimes of ethylene and propylene are essentially determined by HO. Temperature dependent HO rate coefficients are reasonably well known for many hydrocarbons. In general, the 2 sigma uncertainty for HO + alkane rate constants at room temperature is about 30% [Atkinson, 1994]. Table 1 lists the rate coefficients used in this paper. Rate constants below room temperature for i-pentane, hexane, 2-methylpentane, 3-methylpentane, and heptane were calculated from structure activity relationships [Atkinson, 1987].

Since HO radical concentrations vary with insolation, hydrocarbon lifetimes change significantly with season and latitude. Most of the data presented here were collected over a relatively short time interval (about a month) so that a monthly average HO concentrations can be used from model estimates [Spivakovsky et al., 1990]. The uncertainty in HO concentration is likely a large source of uncertainty in the estimated hydrocarbon lifetimes, but we wish to use local hydrocarbon lifetimes rather than rate coefficients so that we may make an easy comparison with Junge's relationship and with atmospheric mixing timescales and transport times. If lifetimes are short compared to mixing and transport timescales, we anticipate that local sources of hydrocarbons may be important in influencing concentration trends. Using lifetimes also incorporates the fact that alkenes are removed by both O₃ and HO so that the relative abundance of both these oxidants will be important in shaping alkene distributions and in turn how alkene variability relates to the variability of simple alkanes. For the NARE 1993 data sets an HO concentration of 1×10^6 molecules cm⁻³ was assumed, reflecting an approximate, average HO concentration for a midlatitude summer. For the Boulder data set a concentration of 1×10^5 molecules cm⁻³ was used based on average latitudinal HO concentrations reported by Spivakovsky et al. [1990]. Estimating lifetimes for the Alert data is very difficult as Alert itself is in darkness at this time of year. Lifetimes of these hydrocarbons will be determined along the sunlit portion of the transport path from the source. Since these sources will be located in mid-latitudes, 45°-60°N, we assume an HO concentration of 1×10^4 molecules cm⁻³ based on the model concentrations of Spivakovsky et al. [1990]. The uncertainty in the estimated lifetimes does not affect the trends observed in the data sets, only our comparison between mixing timescales and lifetimes. Table 2 lists the estimated local lifetimes for the above locations.

Results

North Atlantic Regional Experiment 1993

Table 3 lists a few pertinent details of the NARE 1993 hydrocarbon data sets considered in this paper. In Plate 1 the cumulative distributions of ethane, propane, n-butane, and i-pentane are compared. All these species were reported above their respective labs' detection limits in all samples, and an informal intercomparison during NARE 1993 showed good agreement for the alkanes between the UCI and York groups. Two ethane data (13.3 and 13.9 ppbv) from the Twin Otter are

Table 1. HO Radical Rate Coefficients for Selected Hydrocarbons

| Species | cm ³ molecule ⁻¹ s ⁻¹ | Temperature(K) | Reference |
|------------------------|--|----------------|-----------|
| Ethane | $1.03 \times 10^{-11} \exp(-1110/T)$ | 212-380 | 1 |
| Propane | $1.01 \times 10^{-11} \exp(-660/T)$ | 212-380 | 1 |
| n-butane | $2.04 \times 10^{-17} T^2 \exp(85/T)$ | 212-380 | 1 |
| i-butane | $9.32 \times 10^{-18} T^2 \exp(275/T)$ | 212-380 | 1 |
| n-pentane | $3.13 \times 10^{-17} T^2 \exp(115/T)$ | 212-380 | 1 |
| i-pentane | 3.9×10^{-12} | 298 | 2 |
| Hexane | 5.61×10^{-12} | 298 | 2 |
| 2-methylpentane | 5.6×10^{-12} | 298 | 2 |
| 3-methylpentane | 5.7×10^{-12} | 298 | 2 |
| Heptane | 7.15×10^{-12} | 298 | 2 |
| Ethylene | $1.96 \times 10^{-12} \exp(438/T)$ | <425 | 2 |
| Propylene | $4.85 \times 10^{-12} \exp(504/T)$ | <425 | 2 |
| Benzene | $3.58 \times 10^{-12} \exp(-280/T) \{k_{\infty}\}$ | 235-355 | 3 |
| Toluene | $1.81 \times 10^{-12} \exp(355/T) \{k_{\infty}\}$ | 213-324 | 2 |
| m-xylene | 2.36×10^{-11} | 250-315 | 2 |
| o-xylene | 1.37×10^{-11} | 296-320 | 3 |
| Ethylbenzene | 7.1×10^{-12} | T<320 | 3 |
| Acetone | $5.34 \times 10^{-18} T^2 \exp(-230/T)$ | 240-1217 | 2 |
| Acetylene ^a | $k_0 = 5 \times 10^{-30} (T/298)^{-1.5}$ | | 3 |
| | $k_{\infty} = 9.4 \times 10^{-12} \exp(-700/T)$ | | 3 |
| | $F_c = \exp(-T/580) + \exp(-2330/T)$ | | 3 |

References: 1, Talukdar [1994]; 2, Atkinson [1994]; 3, Atkinson [1989].

^aReaction significantly within fall-off region at 760 torr air.

off scale and are not shown in the figure. In general, the data from the Azores was the most nearly lognormal in nature. Obvious differences in distribution patterns between species at a given site were observed. For instance, the distinct kink in the n-butane and i-pentane distribution at Sable Island is absent in the propane distribution. The kink appears to demark two different distributions, suggesting the influence of different source types.

While it is difficult to identify the different source types at each location, at Sable Island it is likely that the two dominant source influences are urban and industrial emissions from the eastern United States and Canada and emissions from petroleum sources, either natural seeps or the oil production platform located some 40 km to the southwest of the island [cf. Wang et al., 1996]. The petroleum source is likely reflected in Sable Island's relatively high n-butane and i-pentane mixing ratios at the lowest quantiles. Minimum values for these species were even higher than those observed at Chebogue Point, a site much closer to the large anthropogenic sources of North America. An indicator of the nonurban nature of this source is the significantly higher i-butane to n-butane ratio at Sable Island compared to the other NARE sites. In Figure 1a the i-butane to n-butane ratio is plotted versus n-butane mixing ratios for the NARE, Boulder, and Alert data sets. These data are shown in histogram form with Gaussian curve fits in Figure 1b. The data excluding Sable Island define a relative tight distribution around a median of 0.51. A Gaussian fit to the data yielded a mean of 0.49 and a standard deviation of 0.11. The ratio at Sable Island is significantly larger; the median value calculated from the data is 0.91, while the Gaussian fit yielded a mean of 0.85 and a standard deviation of 0.33. A ratio of 0.49 is typical of the emissions from well mixed urban environments in North America (D.D. Parrish et al., manuscript in preparation 1997).

Interestingly, some very low ethane mixing ratios were observed at Sable Island, lower than those observed at the Azores. Four of these very low mixing ratios were from samples collected on September 4 and 5, following the passage of hurricane Emily. Ethane mixing ratios at this time were more

Table 2. Estimated HO Photochemical Lifetimes in Days

| Species | Summer Data ^a | Winter Data ^b | Alert (Winter) ^c |
|-----------------|--------------------------|--------------------------|-----------------------------|
| Ethane | 47 | 655 | 9040 |
| Propane | 10.5 | 129 | 1560 |
| n-butane | 4.8 | 56 | 630 |
| i-butane | 5.6 | 61 | 650 |
| n-pentane | 2.8 | 33 | 370 |
| i-pentane | 3.0 | 29 | 290 |
| Hexane | 2.1 | 23 | 250 |
| 2-methylpentane | 2.1 | 22 | 220 |
| 3-methylpentane | 2.0 | 20 | 200 |
| Heptane | 1.6 | 19 | 200 |
| Ethylene | 1.4 | 12 | 105 |
| Propylene | 0.44 | 3.8 | 33 |
| Benzene | 8.3 | 90 | 980 |
| Toluene | 1.9 | 17 | 160 |
| m-xylene | 0.49 | 4.9 | 49 |
| o-xylene | 0.84 | 8.5 | 850 |
| Ethylbenzene | 1.6 | 16 | 163 |
| Acetone | 56 | 675 | 8400 |
| Acetylene | 14.2 | 206 | 2900 |

^a Assumes 298 K and HO = 1×10^6 molecules cm⁻³ for NARE region data.^b Assumes 273 K and HO = 1×10^5 molecules cm⁻³ for Boulder winter data.^c Assumes 253 K and HO = 1×10^4 molecules cm⁻³.

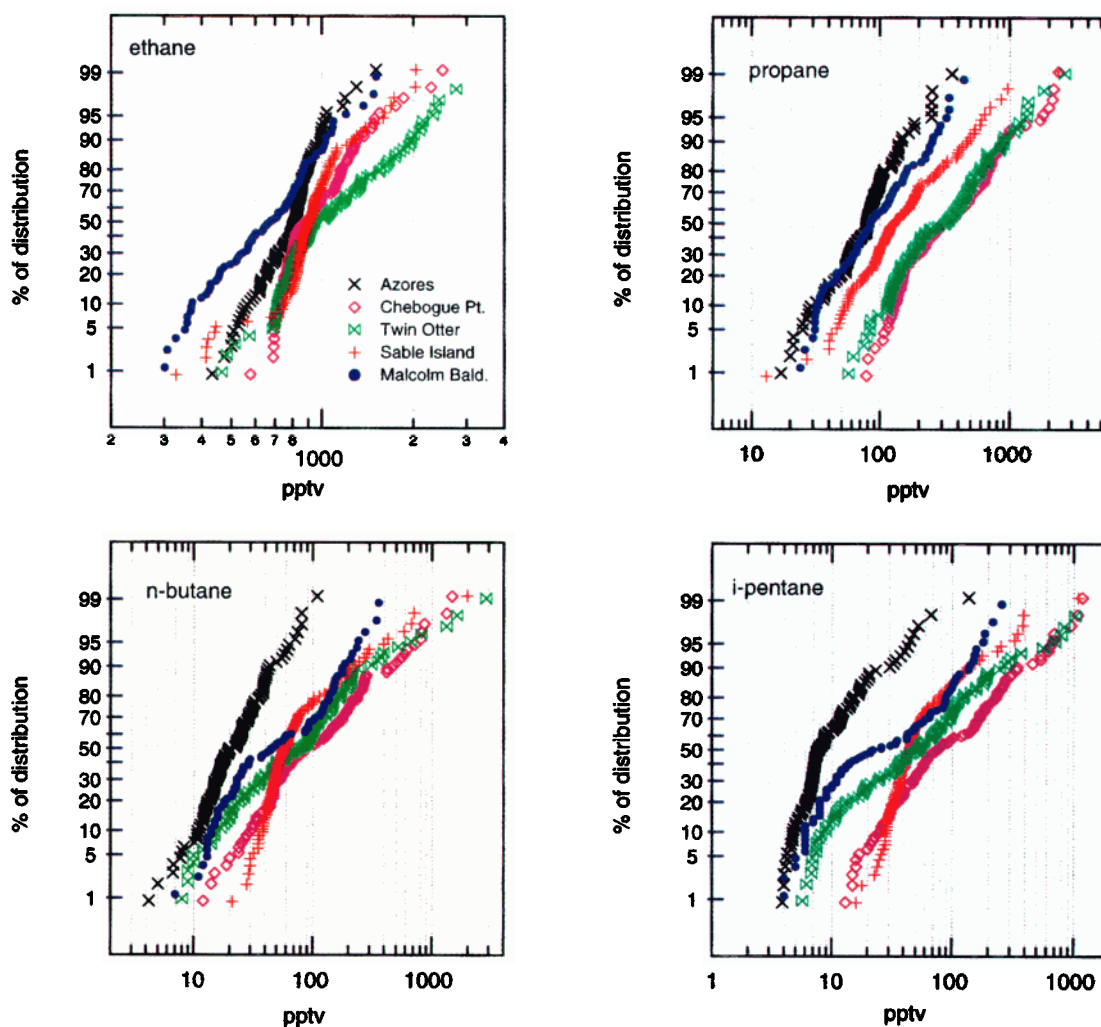
Table 3. NARE 1993 Hydrocarbon Sampling Locations and Observed Median Mixing Ratios (pptv) of Light Alkanes

| | Chebogue Point | Twin Otter | Sable Island | Malcolm Baldrige | Azores |
|-----------|--------------------|--------------------|---------------------|---------------------------------|--------------------|
| Platform | ground site | aircraft | ground site | ship | ground site |
| Location | 43.75°N 66.12°W | Cheb. Point area | 43.93°N 60.02°W | central Atlantic 5°S to 63°N | 38.73°N 27.32°W |
| Period | Aug. 5 to Sept. 12 | Aug. 12 to Sept. 6 | Aug. 15 to Sept. 16 | July 7 to Sept. 20 | Aug. 3 to Sept. 2 |
| Samples | 113 | 107 | 118 | 88 | 114 |
| Ethane | 895 | 949 | 907 | 680 | 817 |
| Propane | 316 | 323 | 130 | 84 | 80 |
| n-butane | 89 | 81 | 59 | 47 | 22 |
| i-pentane | 75 | 54 | 45 | 26 | 7.8 |

typical of average tropical values observed by the *Malcolm Baldrige* (430 pptv for <20°N) and of tropical values reported in the literature [cf. Singh and Zimmerman, 1992]. The two lowest ethane values observed in NARE 1993 (310 and 307 pptv) were from samples collected on the *Malcolm Baldrige* during September 10 when the ship was at 40°N 43°W. The last recorded position of Emily was for September 6 when the depression was at 39.8°N and 49.4°W, and it appears

that these anomalously low ethane values were also associated with the storm.

Some other general features can be noted. The remotest locations, the Azores and *Malcolm Baldrige*, displayed the lowest alkane medians, consistent with the large distance from continental emissions for these sampling locations. The difference in medians between near source and remote locations generally increased with increasing hydrocarbon

**Plate 1.** Cumulative distribution plots for ethane, propane, n-butane, and i-pentane for the NARE 1993 data sets.

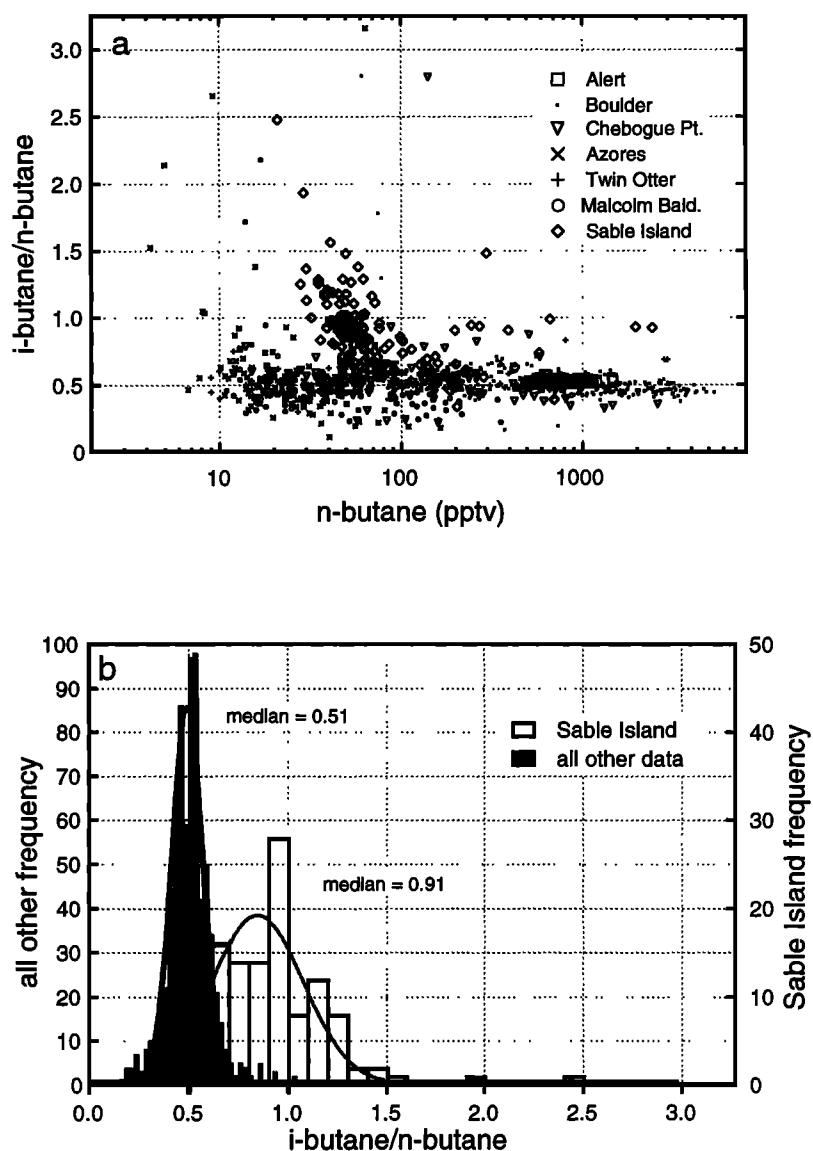


Figure 1. (a) The i-butane to n-butane ratio versus the n-butane mixing ratio. (b) Histograms of the i-butane to n-butane ratios with their respective Gaussian fits.

reactivity. For example, the medians for ethane, propane, n-butane, and i-pentane were 1.1, 4.0, 4.0, and 9.6 times higher at Chebogue Point than the Azores. The relatively large difference in propane medians may be attributed to propane emissions from gas storage facilities in Yarmouth, Nova Scotia, influencing the Chebogue site. For a given location the most reactive species also displayed the greatest dynamic range. At Chebogue Point i-pentane mixing ratios spanned 2 orders of magnitude, while ethane mixing ratios displayed only a factor of 4 spread. These general features are consistent with our intuitive expectation that the most reactive species would display the greatest spatial and temporal variability. In the following section the Junge relation will be compared to hydrocarbon variability versus lifetime trends. Our measure of hydrocarbon variability is the standard deviation of the \ln of the mixing ratios, denoted as $s_{\ln x}$.

Figure 2a illustrates the dependence of $s_{\ln x}$ on photochemical lifetime for the Chebogue Point and Twin

Otter data sets, both collected over southern Nova Scotia. A larger variability was seen in the Twin Otter data, driven in part by collection of two samples near Yarmouth, Nova Scotia with very high mixing ratios of all species. The trend through C_2 – C_4 alkanes, acetylene, and benzene are shown for both data sets. The Twin Otter data define a more coherent trend with C_5 alkane variability departing only slightly from the trend line. For Chebogue Point, the benzene and propane points appear to be below and above the general trend, respectively. Hydrocarbons more reactive than C_4 alkanes fall significantly below the trend line. Also shown in Figure 2a is the Junge relation. All of the data fall below this curve.

In Figure 2b the data from the more remote NARE sites are shown. These locations are far enough removed from large continental hydrocarbon sources that their $s_{\ln x}$ patterns should reflect well processed air. Compared to the near source sites, the $s_{\ln x}$ values for these sites were lower. Sable Island and the Azores displayed the lowest variability amongst the NARE

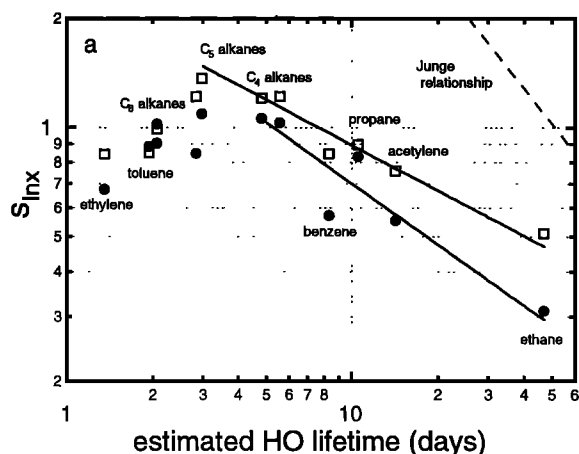


Figure 2a. Standard deviation of the ln-transformed data ($s_{\ln x}$) versus lifetime for Chebogue Point (circles) and the Twin Otter aircraft (squares) from NARE 1993. Least squares regression fits through the C_2 - C_4 alkanes, acetylene, and benzene are shown (Chebogue Point: $s_{\ln x} = 2.54 \tau^{-0.56}$; Twin Otter: $s_{\ln x} = 2.33 \tau^{-0.42}$). The Junge relationship is shown as the dashed line.

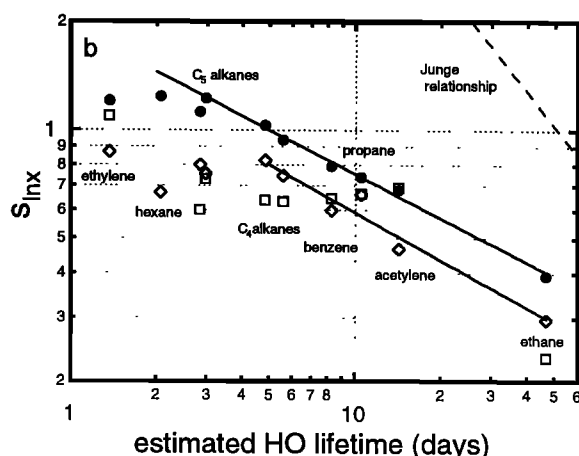


Figure 2b. Standard deviation of the ln-transformed data ($s_{\ln x}$) versus lifetime for Sable Island (diamonds), the *Malcolm Baldrige* (circles), and the Azores (squares) data sets from NARE 1993. The least squares regression fit through the C_2 - C_4 alkanes, acetylene, and benzene is shown for Sable Island and the *Malcolm Baldrige* (Sable Island: $s_{\ln x} = 1.61 \tau^{-0.44}$; *Malcolm Baldrige*: $s_{\ln x} = 1.91 \tau^{-0.40}$).

sites. While the C_2 - C_4 alkanes, acetylene and benzene define a coherent trend at Sable Island, no trend is apparent in the Azores data. In fact, variability decreases slightly from acetylene to C_5 alkanes. In contrast, the *Malcolm Baldrige* data set defines a strong trend from C_2 to C_5 alkanes and displays the most coherence of all the NARE sites. The variation in these data is driven in part by the latitudinal gradient of these species.

Boulder, Colorado

For a period of about 2 weeks in February 1991, hourly samples were collected from a hilltop site overlooking the town of Boulder [Goldan et al., 1995]. This site can receive very fresh pollution from the Denver-Boulder metropolitan area and also very clean air when winds are from the west. Reactive species like toluene displayed over a factor of 100 range in mixing ratio. In Figure 3 $s_{\ln x}$ versus lifetime is shown. The low apparent variability for all the xylene isomers is a result of roughly 10% of the data falling below the limit of detection, so that the full dynamic range and hence variability was not quantified. Again, the Junge relation does not fit the data. At this site, the $s_{\ln x}$ values are above the Junge relationship for the less reactive species and below it for the more reactive. Thus a much flatter dependence is observed. However, it should be noted that the data are closer to the Junge relationship in Figure 3 than in Figure 2 primarily due to the longer winter lifetimes rather than greater variability.

Polar Sunrise Experiment 1992

The motivation for including this data set is to see if the effect of longer local lifetimes by virtue of much lower HO concentrations produces a pattern consistent with Junge's relationship. In Figure 4a it can be seen that the Alert winter

data define a strong trend extending from C_2 to C_7 alkanes but exhibit a much weaker dependence on τ than the Junge relationship. Surprisingly, ethylene and propylene fall along this trend if only their HO lifetimes are considered. Given the low HO concentration expected in high latitude winters, their lifetimes are likely to be determined by reaction with O_3 . Assuming 40 ppbv of O_3 and an HO concentration of 1×10^4 molecules cm^{-3} , the estimated lifetimes are 26.5 days for ethylene and about 3.2 days for propylene. These lifetimes are indicated by the open circles in Figure 4a. The plot suggests the mixing ratio variability is being driven by the variation in their HO loss rate. The simplest explanation is that our assumed average HO concentration of 1×10^4 molecules cm^{-3} is too low relative to a 40 ppbv ozone background. Using

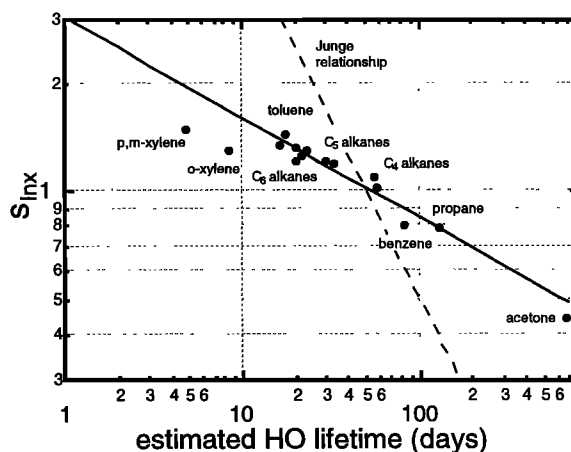


Figure 3. Standard deviation of the ln-transformed data ($s_{\ln x}$) versus lifetime for a 2 week period in February 1991 at Boulder, Colorado. The least squares regression fit is through acetone to ethylbenzene and is given by the expression $s_{\ln x} = 3.04 \tau^{-0.28}$.

local lifetimes determined by an average HO concentration of 1×10^5 molecules cm^{-3} and a 40 ppbv ozone concentration yields a good fit to all species; $s_{\text{Inx}} = 0.74 \tau^{-0.27}$. In support of the Alert data, the results from Hov et al., [1989] are shown in Figure 4b where relative standard deviation is plotted against the same estimated HO lifetimes used in Figure 4a. These data are from samples collected in stainless steel canisters aboard a weather ship in the North Atlantic (66°N) between late February and mid-March, a time and place similar to the Alert data. A well correlated trend between variability and HO lifetime was observed for C_2 to C_5 hydrocarbons, including ethylene. For reasons unknown, acetylene and propylene appear as distinct outliers. The RSD dependence on τ is similar to the Alert data, although the overall variability is higher. For the Alert data, the RSD dependence on τ is the same as for the s_{Inx} statistic. The Arctic data suggest that variability-lifetime relationships may be a useful tool for inferring the

average relative abundance of tropospheric oxidants such as ozone and HO. However, it must be noted that olefin measurements are notorious for sampling artifacts and other analytical difficulties and it would not be circumspect to draw strong conclusions from this data regarding the inferred abundance of HO.

Discussion

With the exception of the Azores data, a clear trend between the standard deviation of the ln-transformed data (s_{Inx}) and photochemical lifetime was observed for species with lifetimes greater than about 5 days. Table 4 summarizes the values of s_{Inx} for the less reactive hydrocarbons, and Table 5 summarizes the parameters and 1σ uncertainties of the regression fit to $s_{\text{Inx}} = A \tau^{-b}$ for the different sites. The dependence on τ ranged from a low of $\tau^{-0.28}$ for the Boulder data to $\tau^{-0.56}$ for the Chebogue Point data. The uncertainty in the HO lifetime does not affect the dependence on τ , only the value of the coefficient A. Combining all the NARE data yields a trend similar to the individual sites. Thus the combined spatial and temporal trends defined by the NARE sampling locations were similar to each location's temporal trend, with the exception of the Azores. The sites farthest removed from large urban and industrial sources of hydrocarbons, Alert and the Azores, displayed the lowest variability. While the Alert data displayed a strongly correlated trend over a wide range of hydrocarbon reactivities, the Azores data did not display the expected tendency of increasing variability with increasing reactivity. None of the data from any of the sites fit the Junge relationship. The exponential model cannot describe two general features of the hydrocarbon trends: (1) species with lifetimes shorter than a few days displayed low variability given the trend of longer-lived species, and (2) for long-lived species a highly correlated trend was observed over a wide range of lifetimes (about a factor of 100 spread in the Arctic) but with a much weaker dependence on τ than the Junge relationship.

One possible cause for reactive species displaying a low variability is that local emissions influenced the data. The variability pattern at the Azores in Figure 2b looks similar to that observed at York University campus, shown in Figure 5, for a set of samples collected during the summer. The campus is located in northern metropolitan Toronto and for the most part is surrounded by urban and industrial sources of hydrocarbons. Occasionally, reasonably low mixing ratios of reactive species can be observed at the site during northerly flow. Figure 5 shows that the hydrocarbons propane through to nonane

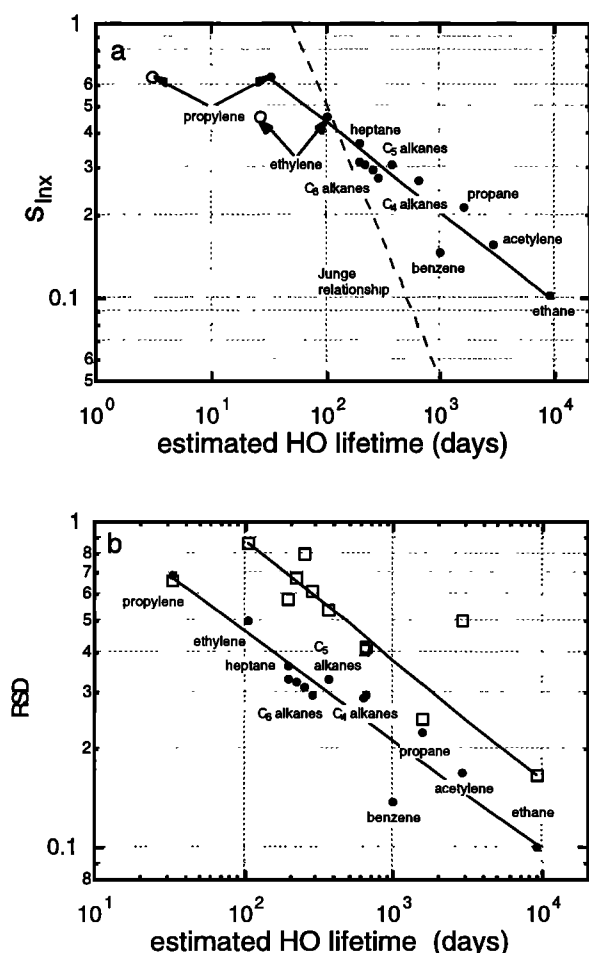


Figure 4. (a) Standard deviation of ln-transformed data (s_{Inx}) versus lifetime for data collected during the dark period (January 21 to March 23) at Alert, N.W.T., during the Polar Sunrise Experiment 1992. Solid circles indicate HO lifetimes only. Open circles are estimated lifetimes resulting from both reaction with HO and O_3 . The least squares regression fit through the C_2 – C_7 alkanes and acetylene is shown and is given by $s_{\text{Inx}} = 1.96 \tau^{-0.33}$. (b) Relative standard deviation versus lifetime for data collected during the dark period at Alert during the Polar Sunrise Experiment 1992 (circles; $\text{RSD} = 2.16 \tau^{-0.33}$) and from Hov et al., [1989] (squares; $\text{RSD} = 4.8 \tau^{-0.37}$).

Table 4. The Variability Statistic s_{Inx} for Light Hydrocarbons at Different Sites

| Site | Ethane | Acetylene | Propane | n-butane |
|------------------|--------|-----------|---------|----------|
| Alert | 0.103 | 0.158 | 0.213 | 0.265 |
| Boulder | NA | NA | 0.793 | 1.09 |
| Chebogue Point | 0.312 | 0.554 | 0.829 | 1.06 |
| Twin Otter | 0.510 | 0.760 | 0.898 | 1.21 |
| Sable Island | 0.296 | 0.468 | 0.662 | 0.822 |
| Malcolm Baldrige | 0.394 | 0.680 | 0.738 | 1.03 |
| Azores | 0.233 | 0.692 | 0.665 | 0.639 |

NA, not available

Table 5. Fit Parameters for the Equation $s_{\ln x} = A \tau^{-b}$

| Site | A | $\pm \sigma_A$ | b | $\pm \sigma_b$ | Reactivity Range |
|------------------|----------|----------------|------|----------------|-------------------------|
| Alert | 1.96 | 0.24 | 0.33 | 0.023 | ethane to propylene |
| Boulder | 3.04 | 0.24 | 0.28 | 0.023 | acetone to ethylbenzene |
| Chebogue Point | 2.54 | 0.77 | 0.56 | 0.15 | ethane to n-butane |
| Twin Otter | 2.33 | 0.30 | 0.42 | 0.066 | ethane to n-butane |
| Sable Island | 1.61 | 0.22 | 0.44 | 0.061 | ethane to n-butane |
| Malcolm Baldrige | 1.91 | 0.085 | 0.40 | 0.021 | ethane to n-butane |
| Azores | no trend | | | | |
| All NARE sites | 2.23 | 0.058 | 0.43 | 0.12 | ethane to n-butane |

displayed no systematic increase in variability. The expected variability trend appears to be suppressed by continuous emissions around the site. The similarity to the Azores trend is interesting, and it is reasonable to suspect that local emissions on the island have influenced the data. Peterson et al. [this issue] observed a distinct local influence on daytime oxides of nitrogen levels at the site, supporting our suspicion regarding hydrocarbons since canisters samples were collected only during the day. While hydrocarbon mixing ratios at the Azores were very low and not obviously influenced, a small local source of fresh emissions may have been enough to obfuscate

the expected variability trend for species more reactive than acetylene.

This source proximity problem may be the reason that the C_5 alkanes and other reactive species in general displayed low variability in the NARE data sets. For instance, Sable Island appears to have been influenced by petroleum emissions. This source has influenced the C_5 alkanes and hexane by suppressing their variability via skewing mixing ratios for the lowest quantiles to higher values. Interestingly, while the C_4 alkane mixing ratios also appear to have been influenced by this source, their variability fits the trend described by the longer-lived species. Reactive species at Chebogue Point and in the Twin Otter data also displayed low variability. It would appear that species with lifetimes short compared to atmospheric dispersion timescales display a variability that is more strongly influenced by “local sources” than longer-lived species which integrate sources over a much longer transport path. Just how strong these local sources must be to influence trends is not evident, but clearly species with low mixing ratios will be the most affected. Note that the data sets with the weakest dependence on τ (Boulder, Alert) were winter data that displayed the strongest correlation over the widest range of lifetimes. The wide range of hydrocarbon reactivities that fit the trend suggest the diminution of the local source effect observed in the summertime NARE sites. This makes sense because wintertime concentrations are much larger than in summer and thus would be less prone to be significantly influenced by small “local” emissions. In view of this apparent source proximity problem, the variability trend of *Malcolm Baldrige* data set is probably the best representation of the remote Atlantic pattern.

There are, however, several possible analytical reasons for low variability that must be acknowledged. One important analytical issue is that of coelution. For instance, benzene variability in the York University data may be masked by a coeluting species with a much longer lifetime and hence lower variability. This would suppress the benzene variability and may explain why the York benzene data generally exhibit a lower variability than the C_2 - C_4 alkane trend. Ethylene artifacts arising from sample storage in canisters may also be confounding trends. These variability plots can be used to advantage for testing the validity of measurements if indeed a variability trend is expected for the species.

That none of the data fit the Junge relationship is noteworthy. The difference between the hydrocarbon trends and the Junge relationship is likely attributable to differences in source-sink distributions, an influence discussed by Hamrud [1983], and to the general influence of atmospheric mixing which changes the relative abundance of hydrocarbons in a

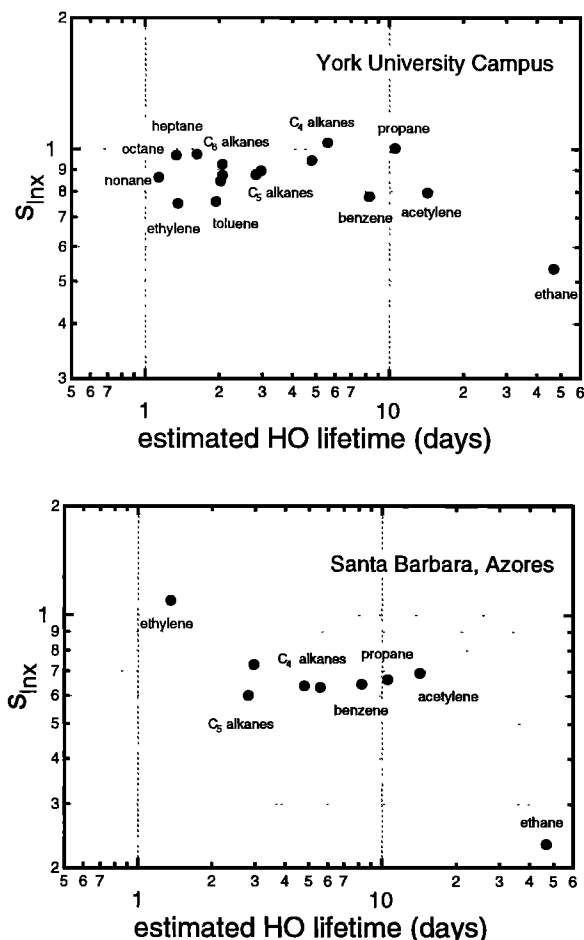


Figure 5. Standard deviation of ln-transformed data ($s_{\ln x}$) versus lifetime for data collected during the summer at (top) the York University campus in Toronto and on (bottom) Santa Barbara in the Azores.

manner not predicted by chemical kinetics [McKeen et al., 1990]. A dependence weaker than the inverse relationship given by equation (4) suggests the influence of atmospheric mixing. This weak dependence on lifetime is similar to that observed for relationships between the logs of hydrocarbon ratios, where the slope defined by the data is smaller than the chemical kinetic slope [Parrish et al., 1992; McKeen and Liu, 1993]. The dependence on τ may thus be a source of information as to relative importance of oxidation and dispersion in determining hydrocarbon concentrations. A variability pattern from a global hydrocarbon distribution would be a better comparison against the Junge relationship, which was principally determined from long-lived species that integrate over a more global source-sink distribution. However, hydrocarbon variability plots from a particular location should be a useful diagnostic for regional 3-D models. It would be desirable to apportion hydrocarbon variability between variability in loss processes and source variability in the sampled air parcels, but a lack of a thorough theoretical treatment of this problem inhibits further interpretation of the hydrocarbon data.

Establishing a variability pattern for hydrocarbons has two important practical applications. Firstly, it allows one to evaluate the overall hydrocarbon data set for consistency. One would expect, given the strongly correlated trends amongst C_2 - C_8 hydrocarbons at Boulder and Alert, that other "ideal" sites would display similar behavior. Deviations of particular hydrocarbons from the trend may point to analytical problems such as poor blanks or canister artifacts, or reveal an instrument to be incapable of quantifying the dynamic range of a particular species. Such problems are difficult to discern by simply looking at mixing ratios or correlations between species. The variability plot also provides a more quantitative description of a site's remoteness since "local" emissions suppress variability. A truly remote sight would be expected to display a strongly correlated trend over a wide range of lifetimes throughout the year.

Second, a coherent variability pattern would allow one to contrast the behavior of alkanes with unsaturated species such as alkenes, acetylene and chlorinated ethylenes. If alkene variability is expected to lie along the same trend defined by the alkanes, acetylene and benzene, then variability-lifetime relationships may provide a novel method for estimating HO concentrations relative to those of O_3 . In addition, anomalously large variability for unsaturated species may indicate the presence of Br-atoms in polluted marine boundary layer environments, a condition that may generally exist outside of the arctic as postulated by Sander and Crutzen [1996]. Such an experiment would best be carried out in winter or fall when HO concentrations are low and a more coherent s_{Inx} versus τ_{HO} trend is likely to be observed.

The role of Cl-atoms in the non-Arctic marine boundary layer has recently become topical, and changes in hydrocarbon relative abundance have been used to infer Cl-atom signatures in remote marine environments [Singh et al., 1996; Wingenter et al., 1996]. In general, Cl + alkane rate coefficients are about 100 times larger than HO + alkane rate coefficients [Hooshiyar and Niki, 1995], so that a relatively small Cl-atom concentration can make a significant difference to alkane lifetimes. Benzene, however, reacts very slowly with Cl; the Cl + benzene rate coefficient is about a factor of 10 smaller than HO + benzene [Atkinson and Aschmann, 1985; Wallington et al., 1988]. Differences in the relative reactivities between n-

and iso-alkanes can also be used to differentiate HO and Cl-atom kinetics [Jobson et al., 1994]. The question we must ask is, How much scatter can we tolerate in the s_{Inx} versus τ_{HO} trends before admitting the presence of other oxidants? For reasons outlined in the discussion the *Malcolm Baldrige* data are probably the best representation of photochemically processed marine air. These data displayed a highly correlated trend between C_2 - C_4 alkane, acetylene and benzene variability and their HO lifetimes and were unperturbed by local source effects. Including Cl-atom reactions will shift the C_2 - C_4 alkane and acetylene lifetimes to lower values with respect to benzene. Cl-atom concentrations 1000 times lower than HO do not significantly alter the excellent correlation between s_{Inx} and τ for the *Malcolm Baldrige* data. However, Cl-atom concentrations much higher than this significantly degrade the correlation between benzene, acetylene, propane, and ethane, enough to suggest that such concentrations are unlikely given the good fit with HO lifetimes alone.

The topical nature of the role of Cl-atoms in the marine boundary layer is perhaps a little off course given that the spring time Arctic measurements and the more general model study of Sander and Crutzen [1996] suggest that time-integrated Br-atom concentrations are hundreds to thousands larger than that of Cl-atoms and thus would have a much greater impact on marine boundary layer ozone budgets. Br + alkane rate coefficients are extremely small, but Br will add to unsaturated species such as acetylene and ethylene sufficiently rapidly that the variability of these species may be a useful probe for this oxidant. Again, using the *Malcolm Baldrige* data and a "goodness-of-fit" approach, whereby the position of acetylene is evaluated with respect to the trend defined by the C_2 - C_4 alkanes and benzene, we found that a Br-atom concentration equivalent to that of HO would not alter the excellent correlation between these species. For a Br-atom concentration 3 times greater than HO, the acetylene lifetime becomes shorter than propane's and thus begins to appear as an outlier.

We conclude from the relatively strong correlations between s_{Inx} and τ_{HO} for the *Malcolm Baldrige* data that halogen atom reactions (if they indeed existed) did not significantly influence the lifetimes of C_2 - C_4 alkanes, acetylene, and benzene. Given an average HO concentration of 1×10^6 molecules cm^{-3} this implies upper limits of about 1×10^6 and 1×10^3 molecules cm^{-3} for Br-atom and Cl-atom concentrations, respectively.

Conclusion

Observations from a number of locations and different seasons in the mid and high latitudes reveal that hydrocarbon variability is correlated with lifetime but not according to the Junge [1974] relationship. The standard deviation of the ln-transformed data (s_{Inx}) was found to follow the relationship $s_{\text{Inx}} = A \tau^{-b}$ when hydrocarbon lifetimes were longer than about 5 days. The most highly correlated trends were observed for wintertime data sets where a much wider range of lifetimes could be fit by this relation. The exponent b ranged from 0.28 ± 0.023 for data taken in wintertime near an urban area to 0.56 ± 0.15 for a coastal site during NARE 1993. The observed dependence on lifetime is weaker than Junge's relationship and the dependence expected from chemical kinetics given by equation (4). The weaker dependence is likely due to the

influence of atmospheric mixing. Differences between hydrocarbon source-sink distributions and those of the longer-lived species considered by Junge may also contribute to the weaker dependence on lifetime. Hydrocarbon data at Sable Island appear to have been influenced by petroleum emissions associated with an oil production platform located to the southwest and/or natural seeps. The *i*-butane/*n*-butane ratio at Sable Island was significantly larger than the 0.49 ± 0.11 average value determined from the other data sets. Such "local source" effects appear to significantly suppress variability of reactive species and is likely why the Azores data did not display the expected variability trend. Anomalously low ethane mixing ratios for a midlatitude summer were observed for a short period at Sable Island and by the *Malcolm Baldrige*, and coincide with the passage of Hurricane Emily.

Acknowledgments. This work was performed while the author held a National Research Council-NOAA Aeronomy Lab Research Associateship. We thank Stu McKeen and Jerome Weinstock for helpful discussions.

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(Received March 3, 1997; revised May 27, 1997; accepted May 30, 1997.)